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CHEMISORBED SPECIES ON AL (U) TEXAS UNIV AT AUSTIN
DEPT OF PHYSICS J L ERSKINE 12 APR 86 AFOSR-TR-86-0750
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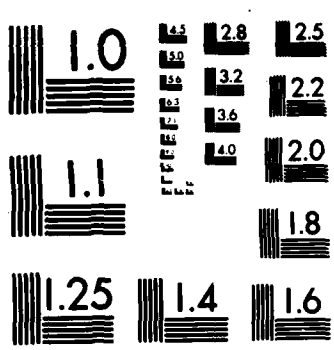

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This project utilized high resolution electron energy loss spectroscopy to investigate chemical processes at metal surfaces. The research during the grant period being reported has been highly successful in: a) advancing the state-of-the-art in instrumentation, b) developing lattice dynamical techniques		

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for calculating the vibrational properties of surfaces and demonstrating the application of these techniques to structure determination, c) exploring the application of vibrational spectroscopy to novel underlayer formation occurring as a consequence of chemisorption at Al and Ti surfaces, d) examining some of the fundamental issues related to scattering mechanisms and selection rules that govern them. Our experiments have also uncovered an interesting relationship between the surface vibrational properties and the order-disorder phase transformation of W(100). This AFOSR sponsored work has attracted attention in the sceintific community as evidenced by an invited review, a number of invited talks and the principal investigator has been asked to prepare a review article entitled, "Electron Energy Loss Spectroscopy," for CRC critical reviews. FINAL REPORT, AFOSR-83-0131, High Resolution Electron Energy Loss Studies of Chemisorbed Species on Aluminum and Titanium.

COMPLETED PROJECT SUMMARY

1. TITLE — High Resolution Electron Energy Loss Studies of Chemisorbed Species on Aluminum and Titanium

2. PRINCIPAL INVESTIGATOR — J. L. Erskine
Physics Department
University of Texas
Austin, TX 78712

3. INCLUSIVE DATES: 1 April 1983 - 31 March 1986

4. GRANT NUMBER: AFOSR-83-0131

5. COST AND FY SOURCE:
$95,463 FY 83
$83,280 FY 84
$20,383 FY 84
$92,825 FY 85

6. SENIOR RESEARCH PERSONNEL: None

7. JUNIOR RESEARCH PERSONNEL:
R. L. Strong (Ph.D. 1984)
J. P. Woods
F. Hadjarab (M.A. 1985)
A. Selledj (M.A. 1985)

8. PUBLICATIONS (REPRINTS ATTACHED)

A. Refereed Journals

1. R. L. Strong and J. L. Erskine, "A New Lens System for Surface Vibrational Spectroscopy at High Impact Energies," Rev. of Sci. Instruments 55, 1304 (1984).

2. R. L. Strong and J. L. Erskine, "A Simple Lattice Dynamical Slab Model for Interpreting Surface Vibrational Spectra: Application of Oxygen on Ni(100) and Ni(111)," Phys. Rev. B31, 6305 (1985).

3. R. L. Strong and J. L. Erskine, "Adsorbate Structure Determination Using Surface Vibrational Spectroscopy," Phys. Rev. Lett. 54, 346 (1985).

4. R. L. Strong and J. L. Erskine, "Underlayer Formation by Oxygen on Al(111) and Ti(0001)," J. Vac. Sci. Technol. A3, 1428 (1985).

5. J. P. Woods and J. L. Erskine, "Experimental Investigation of ß1H on W(100) Using High Resolution Electron Energy Loss Spectroscopy: Bond Distances, Scattering Mechanisms and Impact, Scattering Selection Rules," Phys. Rev. Letters 55, 2595 (1985).

6. J. L. Erskine, "High-Resolution Electron Energy Loss Spectroscopy: Explored Regions and the Frontier," J. Vac. Sci. Technol. (in press).

7. J. P. Woods and J. L. Erskine, "Surface Vibrational Resonances and the Order-Disorder Transformation at the W(100) Surface," J. Vac. Sci. Technol. (in press).

8. J. L. Erskine, "Advanced Electron Optics for Vibrational Spectroscopy," J. Electron Spectroscopy Rel. Phenom. (in press).

B. Technical Reports
AFOSR Interim Report #2: Advanced Electron Optics Feasibility Study

C. Invited Talks and Seminars

"Electron Energy Loss Spectroscopy of Adsorbates at Metal Surfaces," Cornell University, Ithaca, New York, February 23, 1983.

"Electron Energy Loss Studies of Ordered Structures on Crystal Surfaces," J. L. Erskine, 1983 Meeting of the Texas Sections of the American Association of Physics Teachers and the American Physical Society, Denton, Texas, Nov. 18, 1982.

"Surface Vibrational Spectroscopy of Ordered Overlayers on Crystal Surfaces," American Vacuum Society Lecture, Texas A&M University, College Station, Texas, April 24, 1984.

"Electron Energy Loss Studies of Ordered Structures at Metal Surfaces," Physics Department Colloquium, UT Arlington, Arlington, Texas, February 22, 1984.

"High Resolution Electron Energy Loss Study of Ordered Structures at Metal Surfaces," 20th Annual Symposium, The New Mexico Chapter of the American Vacuum Society, Albuquerque, New Mexico, April 17-19, 1984.

"Adsorbate Structure Determination Using Electron Energy Loss Spectroscopy and a Parametrized Lattice Dynamical Slab Model," Forty-Fourth Annual Conference on Physical Electronics, Princeton, NJ, June 18-20, 1984.

"High-Resolution Electron Energy Loss Spectroscopy: Explored Regions and the Frontier," J. L. Erskine, 32nd National Symposium of the American Vacuum Society, Houston, Texas, Nov. 18-22, 1985.

"New Instrumentation for Studying EELS Impact Scattering Cross Sections," J. L. Erskine, Vibrations at Surfaces IV, Bowness-on-Windermere, England, Sept. 15-19, 1985.

"Surface Vibrational Resonances and the Order-Disorder Transformation at the W(100) Surface," J. P. Woods and J. L. Erskine, 32nd National Symposium of the American Vacuum Society, Houston, Texas, Nov. 18-22, 1985.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS

This project utilizes high resolution electron energy loss spectroscopy to investigate molecular level chemical processes at metal surfaces. The research during the grant period being reported in this document has been highly successful in: a) advancing the state-of-the-art in instrumentation (refer to publications #1, 8, and interim report #2), b) developing lattice dynamical techniques for calculating the vibrational properties of surfaces and demonstrating the application of these techniques to structure determination (refer to publications #2 and 3), c) exploring the application of vibrational spectroscopy to novel underlayer formation occuring as a consequence of chemisorption at Al and Ti surfaces (refer to publication #4) c) in examining some of the fundamental issues related to scattering mechanisms and selection rules that govern them (refer to publication #5). Our experiments have also uncovered an interesting relationship between the surface vibrational properties and the order-disorder phase transformation of W(100) (refer to publication #7). Our AFOSR sponsored work has attracted attention in the scientific community as evidenced by an invited review (ref. #6) and a number of invited talks (refer to 8C Invited Talks and Seminars). Based on our contributions to the field, the principal investigator has been asked to prepare a review article entitled, "Electron Energy Loss Spectroscopy," for *CRC critical reviews* (see attached letter).

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January 28, 1986

Dr. J.L. Erskine
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Dear Dr. Erskine:

CRC CRITICAL REVIEWS IN SOLID STATE & MATERIALS SCIENCES is a journal we are publishing under the editorship of Dr. Joe Greene. Because we feel that you have done interesting and impressive work in this area, the Editor(s) has asked me to invite you to author an article on 'High Resolution Electron Energy Loss Spectroscopy'. If you wish to alter this title or suggest an appropriately related one, please contact me.

The author's approach should be a critical review of the important literature recently published in this field, including a synthesis of the findings in relation to the current 'state-of-the-art'. Manuscript length should not exceed 100 doublespaced typed pages, including references, tabular matter and illustrations. Each manuscript is reviewed by an expert referee, usually selected from a list of names submitted by the author.

As the due date for the finished manuscript we suggest November, 1986. If this does not give you adequate time to complete the task, please contact me as soon as possible.

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cc: Dr. Joe Greene

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1304 Rev. Sci. Instrum. 55 (8), August 1984 0034-6748/84/081304-06$01.30

New lens system for surface vibrational spectroscopy at high impact energies

R. L. Strong and J. L. Erskine

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(Received 15 March 1984; accepted for publication 25 April 1984)

The design, characterization, and performance of a new lens system which permits high-resolution electron energy-loss spectroscopy (EELS) studies at high energies is described. The lens system can be adapted to most existing EELS instruments and extends the impact energy range to 300 eV. Electron ray-tracing techniques are used to characterize operating modes of one of the more common EELS optics designs as well as the new lens configuration. The results presented in this paper demonstrate some limitations of matrix optics approaches and the applicability of electron ray-tracing techniques for characterizing the transmission properties, angular profiles, image sizes, and operating modes of EELS spectrometers.

PHYSICAL REVIEW B VOLUME 31, NUMBER 10 15 MAY 1985

Simple lattice-dynamical slab model for interpreting surface vibrational spectra: Application to oxygen on Ni(100) and Ni(111)

R. L. Strong and J. L. Erskine

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(Received 10 September 1984)

A parametrized lattice-dynamical slab model is presented and used to analyze the vibrational properties of oxygen adsorbed on Ni(100) and Ni(111) surfaces. Results obtained from the slab-model technique are compared with corresponding predictions based on a Greens's-function approach to contrast the relative merits of these two methods for obtaining information about vibrational phenomena. The lattice-dynamical slab model is also used to analyze experimental data for several ordered oxygen configurations on the Ni(111) and Ni(100) surfaces, including the proposed pseudobridge site for $c(2\times2)$ oxygen on Ni(100). The results presented indicate that lattice-dynamical calculations can be used not only to test structural models proposed on the basis of experimental measurements or other theoretical calculations, but can also serve as a basis for independent structural determinations (bonding sites and bond lengths) when there is sufficient surface vibrational data to constrain the calculations adequately.

VOLUME 54, NUMBER 4 PHYSICAL REVIEW LETTERS 28 JANUARY 1985

Adsorbate Structure Determination Using Surface Vibrational Spectroscopy

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(Received 26 July 1984)

We show that lattice-dynamical slab calculations and surface vibrational spectroscopy can be used to obtain adsorbate structural parameters directly.

PACS numbers: 68.20.+t, 63.20.Dj, 68.30.+z, 79.20.Kz

VOLUME 55, NUMBER 23 PHYSICAL REVIEW LETTERS 2 DECEMBER 1985

Experimental Investigation of β_1-H on W(100) Using High-Resolution Electron-Energy-Loss Spectroscopy: Bond Distances, Scattering Mechanisms, and Impact-Scattering Selection Rules

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(Received 8 March 1985)

High-resolution electron-energy-loss studies of β_1-H and β_1-D on W(100) are reported for experimental conditions under which the first-order diffracted beam emerges from the crystal. A new vibrational mode is observed and assigned to the asymmetric stretch mode of β_1-H. The results yield an independent new determination of the H-W bond distance. The impact-energy dependence of the new asymmetric stretch mode does not agree with theoretical predictions related to cross sections and selection rules that govern them.

PACS numbers: 68.30.+z, 63.20.Dj, 68.20.+t, 79.20.Kz

 J. Vac. Sci. Technol. A 3 (3), May/Jun 1985 0734-2101/85/031428-04$01.00

Investigation of underlayer formation by oxygen on Al(111) and Ti(0001)

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(Received 12 October 1984; accepted 6 December 1984)

High-resolution electron energy loss spectroscopy is used to investigate the initial stage of oxide formation on Al(111) and Ti(0001) surfaces. Analysis of the O/Al(111) vibrational data based on lattice dynamical slab calculations confirms underlayer formation as a precursor to oxidation. These results help account for some of the novel properties associated with oxygen chemisorption on Al(111) and Ti(0001) surfaces and also illustrate the ability of vibrational spectroscopy to provide surface structure information which complements results of other structure sensitive techniques.

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Running Title: High resolution electron energy loss

High resolution electron energy loss spectroscopy: Explored regions and the frontier

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(Received 22 August 1985; accepted 3 December 1985)

High-resolution electron energy loss spectroscopy (EELS) is rapidly being developed into one of the more useful techniques for probing physical and chemical phenomena at surfaces. Key elements of the technique include high surface sensitivity, the fact that it is a molecular sensitive rather than an atom sensitive spectroscopy, and the direct relationship that exists between experimental data and important surface parameters. New applications of EELS are currently being explored; these applications will be the primary focus of this paper. Recent work which combines EELS measurements with modeling of surface vibrations based on lattice dynamical calculations has shown that this approach can provide useful insight into structural parameters at surfaces. Other experiments aimed at refining our understanding of EELS scattering mechanisms and the selection rules that govern them have yielded some new and unexpected results which will be discussed. Finally, development of a new generation of EELS spectrometers should eventually produce improvements of two to three orders of magnitude in signal levels as well as more precise control of instrument response. These instruments will open up new applications of the EELS technique in areas including the study of technical surfaces and real time studies of surface reaction kinetics. The new spectrometers will also permit more precise studies of fundamental surface phenomena including electron scattering mechanisms.

ADVANCED ELECTRON OPTICS FOR VIBRATIONAL SPECTROSCOPY

J. L. Erskine
Department of Physics, University of Texas, Austin Texas 78712

ABSTRACT

Requirements for a "next generation" high resolution electron energy loss spectrometer for probing surface vibrations are proposed based on several specific applications in which the performance of present generation instruments is marginal or totally inadequate. Prospects of achieving significant improvements are explored and found to be very good for applications which involve studies of impact scattering phenomena. Results of zoom lens ray tracing studies, analysis of electron trajectories and exit plane images in a hemispherical analyzer in relation to multichannel energy detection and studies of electron trajectories near various field terminators are presented. A prototype analyzer / monochromator design is described which will be used to test the model calculations and to extend the applications of EELS to more detailed studies of impact scattering.

SURFACE VIBRATIONAL RESONANCES AND THE ORDER-DISORDER TRANSFORMATION OF THE W(100) SURFACE

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Reconstruction of the clean W(100) surface was originally observed with LEED when the crystal was cooled below room temperature.[1] The reconstructed surface exhibits sharp c(2×2) LEED spots which become weak and diffuse as the sample approaches room temperature.[2] LEED beam broadening and intensity reduction indicate a loss of long range order. MeV ion scattering experiments[3] suggest a structural model with W surface atoms displaced in a random manner corresponding to small domains. This is the first proposed disordered W(100) surface model since surface disorder was dismissed as unreasonable in Ref. 1. Adsorption of hydrogen at room temperature can restore long range order to the surface.[4] Low coverage hydrogen adsorption (0.3 monolayer) on W(100) also yields a c(2×2) LEED pattern, and saturated hydrogen produces a p(1×1) LEED pattern. The saturated surface is commensurate with the bulk, and several models for the low temperature and hydrogen induced c(2×2) surfaces have been proposed.[5,6]

We have investigated the W(100) surface with Electron Energy Loss Spectroscopy (EELS). EELS provides a wealth of information useful in characterizing this surface. Surface contaminants (C, O, CO) are detectable to ~1% monolayer. The dipole modes of low coverage and saturated hydrogen occur at 155 and 130 meV respectively.[6] In Fig. 1 several EEL spectra are shown on a logarithmic intensity scale. With an elastic peak resolution of 7 meV, a new vibrational mode is observed at 26 meV on the hydrogen saturated room temperature surface. The vibrational energy does not shift with

deuterium adsorbtion indicating this mode is an intrinsic vibration associated with the W surface. Similar losses have been observed[7] on Cu(110) and Ni(110). In these cases, it has been proposed that extreme in the longitudinal bulk phonon dispersion within the Brillouin zone (a Van Hove singularity) leads to a gap in the probed density of states, and to the observed surface resonance in the EEL spectra. The longitudinal bulk phonon dispersion curve for W(100)[8] has a corresponding maximum at an energy of 26 meV. The intensity of the loss feature decreases in off specular geometry, characteristic of dipole scattering. A calculation[9] of the phonon density of states for W(100) shows a local maximum near 26 meV for surface vibrations perpendicular to the surface.

A second low energy loss is observed at 36 meV when the clean crystal is cooled to 78°K. The surface has c(2×2) symmetry which can couple surface phonon modes from $\bar{M}$ to $\bar{\Gamma}$ and allow them to be observed in specular scattering geometry. Similar coupling due to ordered adsorbate structures has been observed on Ni(111).[10] The mapping of p(1×1) $\bar{M}$ to $\bar{\Gamma}$ in the c(2×2) surface Brillouin zone is shown in Fig. 1. The observed vibrational energy is above the bulk phonon maximum, indicating that the surface phonon band from $\bar{\Gamma}$ to $\bar{M}$ lies above the bulk continuum. An increase in the surface force constants can cause the surface band to lie above the bulk bands. Phonon band calculations must also include new lattice sums due to the reconstructed surface.

Fig. 1 also shows a room temperature spectrum for clean W(100). Small features near 70, 110 and 155 meV result from low coverage CO, deuterium and hydrogen adsorbed from the background pressure of 2.10^{-11} Torr. There are no losses observed below 45 meV. This result suggests that the clean room

temperature surface is disordered, and therefore, cannot support the bulk phonon mode resonance since the required symmetry is destroyed.

Low coverage hydrogen spectra have not shown any clear low energy features. This is partly due to long signal averaging times needed for the high resolution EEL spectra. The low coverage hydrogen surface is known to be a dynamic surface[4], as the structure changes from commensurate c(2×2) to incommensurate c(2×2) to disordered surface as hydrogen coverage increases. Very careful LEED work will be required in conjunction with single sweep, low signal to noise ratio EELS experiments to study the ordered low coverage hydrogen states.

In summary, high resolution EELS has yielded strong evidence for the disorder-order transition of the W(100) surface. Two distinct low energy loss peaks have been observed and attributed to independent loss mechanisms involving 1) bulk phonon vibrations from the commensurate surface and 2) surface phonon vibrations from the Brillouin zone edge mapped back to the zone center by the reconstructed surface layer. The clean room temperature surface exhibits no phonon modes. This can be attributed to the loss of long range order at the surface.

References

1. K. Yonehana and L. D. Schmidt, Surf. Sci. 25, 238 (1971).

2. T. E. Felter, R. A. Barker and P. J. Estrup, Phys. Rev. Lett. 38, 1138 (1977).

3. I. Stensgaard, L. C. Feldman and P. J. Silvermann, Phys. Rev. Lett. 42, 247 (1979).

4. R. A. Barker and P. J. Estrup, Phys. Rev. Lett. 41, 1307 (1978).

5. A. J. Melmed and W. R. Graham, Appl. of Surf. Sci. 11/12, 470 (1982).

6. M. R. Barnes and R. F. Willis, Phys. Rev. Lett. 41, 1729 (1978); A. Adnot and J. D. Carette, Phys. Rev. Lett. 39, 209 (1977).

7. Joseph A. Stroscio, M. Persson, Simon R. Bare and W. Ho, Phys. Rev. Lett. 54, 1428 (1985).

8. S. H. Chen and B. N. Brockhouse, Solid State Comm. 2, 73 (1964).

9. J. E. Black, Bernardo Laks, and D. L. Mills, Phys. Rev. B 22, 1818 (1980).

10. H. Ibach and D. Bruchmann, Phys. Rev. Lett. 44, 36 (1980).

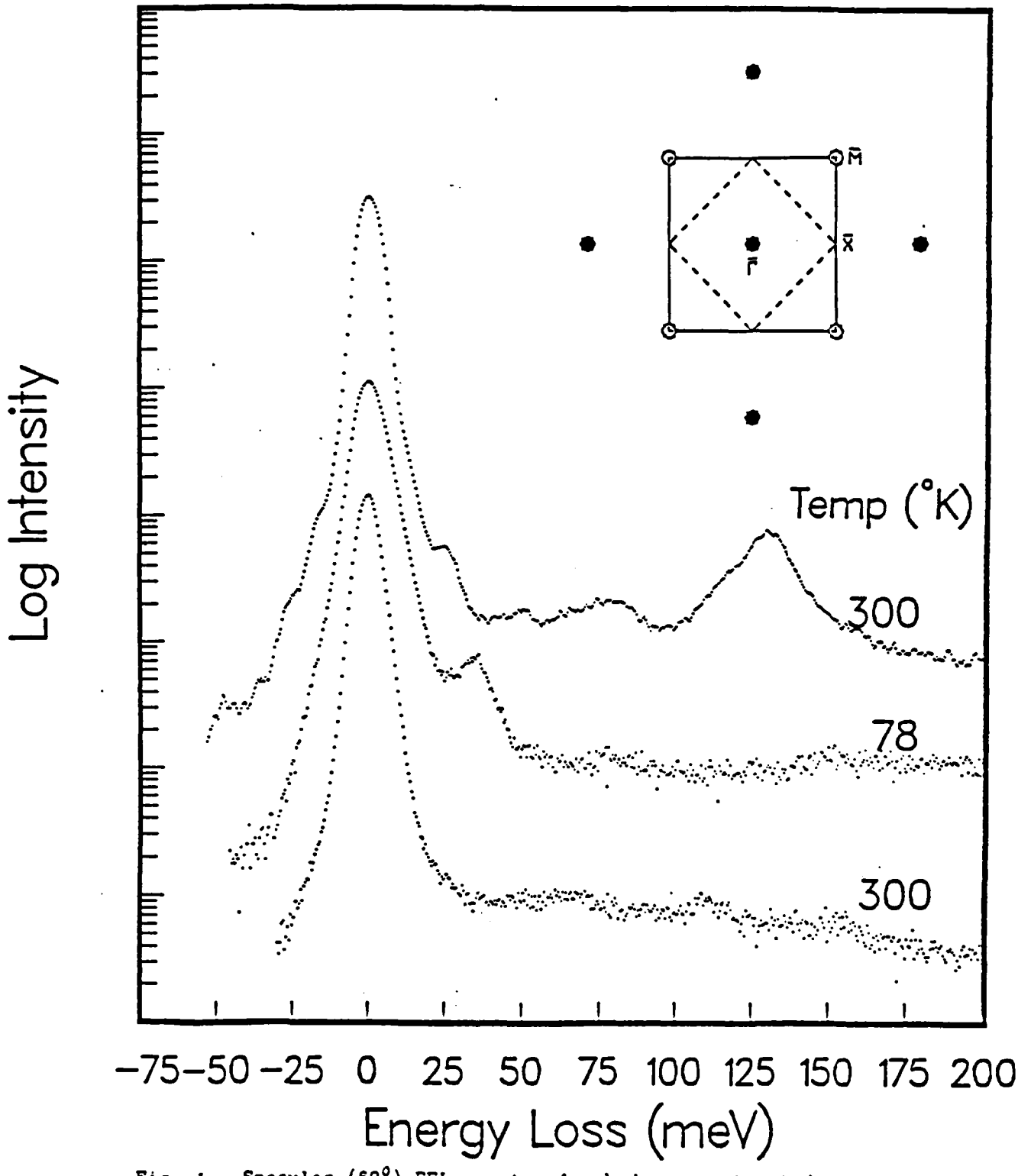

Fig. 1. Specular (60°) EEL spectra for hydrogen saturated surface E_{inc} = 3.9 eV. clean cooled surface E_{inc} = 4.5 eV and clean room temperature surface E_{inc} = 4.2 eV. Insert: Two dimensional LEED spots and Brillouin zones; p(1×1) solid circles and solid line, c(2×2) open circles and dotted line.

END

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